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Fast Detailed Hydrocarbon Analysis of Naphtha

Coen Duvekot
Varian, Inc.

Individual hydrocarbon components of spark-ignition engine fuels and their mixtures can be determined with well known detailed hydrocarbon analysis methods such as ASTM D 5134, D 6729 and D 6730. These methods use long (50 to 100 m), narrow bore capillary (250 µm) columns to meet the high resolution specifications of the methods.

The analysis time, however, usually exceeds two hours. This application note describes a fast DHA method. By using a 40 m x 0.1 mm x 0.2 µm CP-Sil PONA CB column, the analysis time is reduced, depending on the sample type, to 20 to 40 minutes.

Table 1. Peak identification

1 propene	47 1,1-dimethylcyclopentane	93 2,3,3-trimethylhexane
2 iso-butane	48 t-1,3-dimethylcyclopentane	94 p-xylene
3 butane	49 3-ethylpentane	95 3,4-dimethylheptane(L)
4 t-2-butene	50 t-1,2-dimethylcyclopentane	96 2,3-dimethylheptane
5 neo-pentane	51 1-heptene	97 4-ethylheptane
6 c-2-butene	52 2,2,4-trimethylpentane	98 4-methyloctane
7 cyclobutane	53 heptane	99 2-methyloctane
8 iso-pentane	54 c-3-heptene	100 ctc-124-trimethylcyclohexane
9 1-pentene	55 t-3-methyl-2-hexene	101 3-ethylheptane
10 iso-propanol	56 t-2-heptene	102 3-methyloctane
11 pentane	57 c-1,2-dimethylcyclopentane	103 o-xylene
12 t-2-pentene	58 methylcyclohexane	104 1-nonene
13 c-2-pentene	59 1,1,3-trimethylcyclopentane	105 t-1-methyl-4-ethylcyclohexane
14 2-methyl-2-butene	60 ethylcyclopentane	106 c-1-methyl-4-ethylcyclohexane
15 2,2-dimethylbutane	61 2,4-dimethylhexane	107 t-1-me-2-n-propylcyclopentane
16 4-methyl-1-pentene	62 ctc-124-trimethylcyclopentane	108 nonane
17 cyclopentene	63 3,3-dimethylhexane	109 t-1-methyl-2-ethylcyclohexane
18 3-methyl-1-pentene	64 2,3,3-trimethylpentane	110 iso-propylcyclohexane
19 cyclopentane	65 ctc-123-trimethylcyclopentane	111 3,3,5-trimethylheptane
20 MTBE	66 toluene	112 2,2-dimethyloctane
21 2,3-dimethylbutane	67 3-methyl-3-ethylpentane	113 2,5-dimethyloctane
22 2-methylpentane	68 c-1,3-dimethylcyclohexane	114 sec-butylcyclopentane
23 3-methylpentane	69 3,4-dimethylhexane (D)	115 2,6-dimethyloctane
24 2-methyl-1-pentene	70 2-methylheptane	116 2,3,6-trimethylheptane
25 1-hexene	71 4-methylheptane	117 3,3-dimethyloctane
26 hexane	72 3-methylheptane	118 2-methyl-3-ethylheptane
27 t-2-hexene	73 3-ethylhexane	119 n-propylbenzene
28 t-3-hexene	74 1,1-dimethylcyclohexane	120 1-methyl-3-ethylbenzene
29 2-methyl-2-pentene	75 t-1,3-ethylmethylcyclopentane	121 1-methyl-4-ethylbenzene
30 t-3-methylcyclopentene	76 t-1,2-ethylmethylcyclopentane	122 2,5,5-trimethylheptane
31 t-3-methyl-2-pentene	77 1,1-ethylmethylcyclopentane	123 2,3-dimethyloctane
32 1-hexyne	78 t-1,4-dimethylcyclohexane	124 4-methylnonane
33 c-2-hexene	79 cycloheptane	125 1-methyl-2-ethylbenzene
34 2,2-dimethylpentane	80 octane	126 3,3,4-trimethylheptane
35 methylcyclopentane	81 iso-propylcyclopentane	127 3-ethyloctane
36 2,4-dimethylpentane	82 c-12-ethylmethylcyclopentane	128 iso-butylbenzene
37 2,2,3-trimethylbutane	83 c-1,2-dimethylcyclohexane	129 decane
38 benzene	84 2,4-dimethylheptane	130 1,2,3-trimethylbenzene
39 3,3-dimethylpentane	85 4,4-dimethylheptane	131 1-methyl-4-isopropylbenzene
40 cyclohexane	86 2,6-dimethylheptane	132 1-methyl-2-isopropylbenzene
41 t-4-methyl-2-hexene	87 3,5-dimethylheptane	133 1-methyl-3-n-propylbenzene
42 2-methylhexane	88 2,5-dimethylheptane	134 1-methyl-4-n-propylbenzene
43 2,3-dimethylpentane	89 3,3-dimethylheptane	135 1-methyl-4-n-propylbenzene
44 2-methyl-1,5-hexadiene	90 ethylbenzene	136 1,4-diethylbenzene
45 3-methylhexane	91 2,3,4-trimethylhexane	137 1,2-diethylbenzene
46 c-1,3-dimethylcyclopentane	92 ctt-1,2,4-trimethylcyclohexane	138 undecane

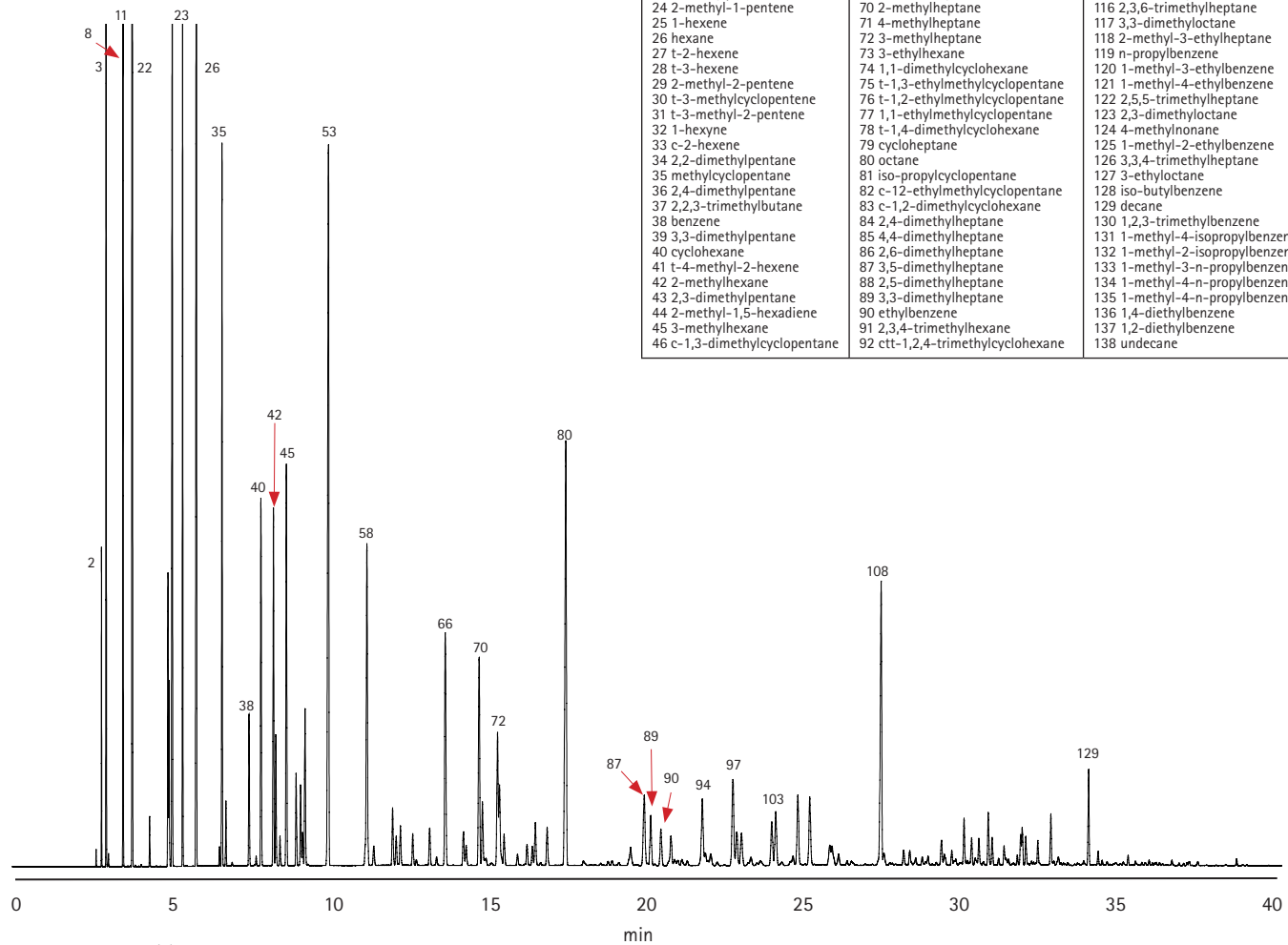

Figure 1. Naphtha (3).

Instrumentation

GC: Varian 450-GC Gas Chromatograph
Injector: Split/splitless with full EFC control
Detector: FID with full EFC control
Autosampler: Varian CP-8400 AutoSampler

Software
GC control and data handling: Galaxie™ Software from Varian
DHA calculations: DHA software fully integrated into Galaxie

Materials and Reagents

Column: Varian CP-Sil PONA CB, 40 m x 0.1 mm x 0.2 µm, (CP910984)
Samples: Light naphtha (1 and 2), naphtha (3)

Conditions

Injector: 1177, split 700:1, 250 °C
Detector: FID, 300 °C
Carrier Gas: Helium, 95 psi
Oven Temp: 35 °C (5 min) @20 °C/min to 45 °C (6 min), @2.5 °C/min to 60 °C (6 min), @5 °C/min to 220 °C (2.5 min)
Inj. Vol: 1 µL

Results and Discussion

A standard sample mixture containing n-alkanes was used to calibrate the software. The retention times of the n-alkanes were used to calculate the retention indices of the sample components. These retention indices were then compared with a database and peaks were assigned accordingly. Table 1 shows some of the components in the database, which now contains more than 450 examples. This approach is very powerful, with virtually all peaks identified. A good example of this is shown in the magnified portion of the chromatogram (from Figure 1), depicted in Figure 2.

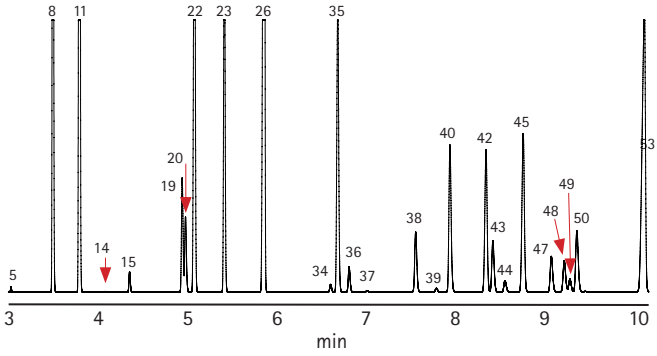

Figure 2. Magnified section of naphtha (3) chromatogram from Figure 1.

The database contains component information such as density, Motor Octane Number (MON) and Research Octane Number (RON) values, and vapor pressure, etc. Together with the chromatographic results, the DHA software makes the appropriate calculations and generates associated results. Different reports, depending on the type of information needed, can also be generated.

In the detailed hydrocarbon report, the weight and volume percent for each component identified is produced (Table 2).

Varian DHA Analyzer hydrocarbon report

Analysis according to FAST DHA

Sample Info	N.A.		
Sample Type	Sample		
Date Analysed	26 Oct 2007, 03:57:41	Date Printed	09 Nov 2007, 12:05:35
Analyst	ADMINISTRATOR	Vial	12
Data File	\Naptha\FastDHA Naptha(3).DATA		
Method	\450 Fast DHA\450 Fast DHA Samples\450-GC Fast DHA.dha		
Description	FastDHA Naptha(3)		
Instrument	GC450 110117		

Detailed Hydrocarbon Analysis

ID	RT	CRT	Index		Name	Area	Area Percent	Weight Percent	Volume Percent
1	2.64	2.64	292.42	*	propene	8.5	0.04	0.06	0.08
2	2.81	2.81	354.44	*	iso-butane	144.0	0.72	0.93	1.13
3	2.95	2.95	400.50		butane	931.8	4.67	5.57	6.53
4	3.03	3.03	410.68		neo-Pentane	6.5	0.03	0.04	0.04
5	3.49	3.49	467.58		iso-pentane	1644.7	8.24	9.07	9.93
6	3.78	3.77	498.75		pentane	2451.6	12.29	13.52	14.65
7	4.06	4.06	516.88		2-methyl-2-butene	1.8	0.01	0.01	0.01
8	4.33	4.33	531.80	*	2,2-dimethylbutane	33.2	0.17	0.18	0.18
9	4.90	4.90	561.18	*	cyclopentane	212.9	1.07	1.17	1.07
10	4.94	4.94	562.90	*	MTBE	144.0	0.72	1.03	0.94
11	5.04	5.02	566.80		2-methylpentane	1096.7	5.50	5.80	6.02
12	5.36	5.36	582.32		3-methylpentane	699.0	3.50	3.70	3.77
13	5.80	5.78	599.78		hexane	1905.2	9.55	9.19	9.46
14	6.52	6.52	622.33	*	2,2-dimethylpentane	16.6	0.08	0.08	0.08
15	6.60	6.60	624.53		methylcyclopentane	633.5	3.18	3.20	2.90
16	6.73	6.73	627.98		2,4-dimethylpentane	55.3	0.28	0.28	0.28
17	6.92	6.92	633.34		2,2,3-trimethylbutane	3.6	0.02	0.02	0.02
18	7.45	7.45	646.95		benzene	150.1	0.75	0.62	0.48
19	7.68	7.68	652.47		3,3-dimethylpentane	9.8	0.05	0.05	0.05
20	7.83	7.83	656.02		cyclohexane	379.0	1.90	1.92	1.67

Paraffins, isoparaffins, olefins, naphthenes, and aromatics were grouped by either weight and/or volume percent in the PIONA report (Table 3).

Varian DHA Analyzer weight percent profile PIONA report

Analysis according to FAST DHA

Sample Info	N.A.		
Sample Type	Sample		
Date Analysed	26 Oct 2007, 05:04:04	Date Printed	09 Nov 2007, 12:11:17
Analyst	ADMINISTRATOR	Vial	12
Data File	\Naptha\FastDHA Naptha(3).DATA		
Method	\450 Fast DHA\450 Fast DHA Samples\450-GC Fast DHA.dha		
Description	FastDHA Naptha(3)		
Instrument	GC450 110117		

Weight Percent Profile

	Saturates			Unsaturates					
Carbon	Cyclic	Iso	Normal	Cyclic	N+ Iso	Aromatics	Oxyg	Unknown	Total
					0.06				**0.06**
		0.90	5.45						**6.35**
	1.17	9.02	13.41		0.01		1.03		**24.63**
	5.13	9.66	9.20			0.62			**24.61**
	5.05	5.51	5.01		0.16	1.55		0.08	**17.35**
	1.48	4.91	3.76			1.54		1.33	**13.03**
	1.15	4.60	2.45		0.05	0.88		2.09	**11.22**
9+		1.63	0.61			0.18		0.32	**2.74**
Total	**13.98**	**36.23**	**39.90**		**0.27**	**4.77**	**1.03**	**3.82**	**100.00**

The properties report combines the analysis results and calculates boiling range information and other properties such as (MON), (RON) and density (Table 4).

Varian DHA Analyzer

Table 4. Properties report

Analysis according to FAST DHA

Sample Info	N.A.		
Sample Type	Sample		
Date Analysed	26 Oct 2007, 05:04:04	Date Printed	09 Nov 2007, 12:05:47
Analyst	ADMINISTRATOR	Vial	12
Data File	\Naptha\FastDHA Naptha(3).DATA		
Method	\450 Fast DHA\450 Fast DHA Samples\450-GC Fast DHA.dha		
Description	FastDHA Naptha(3)		
Instrument	GC450 110117		

Physical Properties

MON Value	57.6	Net Heat	44.2 kJ/g
RON Value	58.6	Gross Heat	48.0 kJ/g
Reid Vapor P.	14.64 mm Hg	Density	0.6903 g/ml

TBP Report

Recovery Percentage 100.0

TBP % OFF	D86 % OFF
IBP -0.5	
5 % 9.5	
10 % 36.1	
20 % 36.5	
30 % 36.5	
40 % 63.3	
50 % 71.8	
60 % 90.0	
70 % 99.2	
80 % 119.4	
90 % 143.0	
95 % 153.5	
FBP 176.1	

The naphtha (3) sample was analyzed many times to demonstrate repeatability. A summary of the results is given in Table 5 and Figure 3, which show excellent results.

Naphtha(3)

Table 5. Summary results of analysis of naphtha (3)

Run	MON	RON	Density (gr/mL)	Hexane Wt%	Heptane Wt%	Benzene Wt%	Toluene Wt%
1	57.3	58.2	0.6889	9.20	5.00	0.62	1.55
2	58.4	59.5	0.6886	9.19	5.02	0.62	1.55
3	58.0	59.0	0.6890	9.19	5.01	0.62	1.55
4	58.6	59.8	0.6888	9.22	5.02	0.62	1.55
5	58.6	59.9	0.6897	9.19	5.01	0.62	1.55
6	58.5	59.7	0.6890	9.23	5.03	0.63	1.56
7	58.6	59.8	0.6892	9.19	5.00	0.62	1.55
8	57.6	58.6	0.6903	9.20	5.01	0.62	1.55
9	57.9	59.2	0.6899	9.23	5.04	0.62	1.56
10	58.4	59.6	0.6890	9.20	5.02	0.62	1.55
11	57.5	58.5	0.6893	9.22	5.05	0.62	1.56
12	58.5	59.7	0.6891	9.24	5.03	0.63	1.56
13	58.5	59.8	0.6883	9.25	5.03	0.62	1.56
14	56.7	57.6	0.6897	9.24	5.08	0.62	1.57
15	58.0	59.2	0.6897	9.22	5.04	0.62	1.56
16	58.0	59.2	0.6891	9.22	5.06	0.62	1.57
17	58.5	59.7	0.6890	9.19	4.99	0.62	1.54
18	58.2	59.2	0.6903	9.21	5.02	0.62	1.55
19	57.6	58.8	0.6893	9.13	4.97	0.62	1.54
20	58.8	59.9	0.6880	9.23	5.03	0.62	1.56
21	58.3	59.4	0.6883	9.24	5.05	0.63	1.56
22	57.4	58.3	0.6895	9.21	5.03	0.62	1.56
23	57.9	58.8	0.6884	9.19	4.99	0.62	1.54
24	58.9	60.1	0.6880	9.19	5.01	0.62	1.55
25	58.7	60.0	0.6875	9.24	5.02	0.62	1.55
Average	58.136	59.26	0.6890	9.210	5.022	0.621	1.554
St.dev.	0.55	0.65	0.0007	0.026	0.024	0.0033	0.0082
RSD%	0.94	1.09	0.10	0.28	0.47	0.53	0.53

The results shown in Table 5 for the hexane and heptane content clearly show that the system is very capable of measuring larger amounts. Peaks are assigned correctly and repeatability is near perfect.

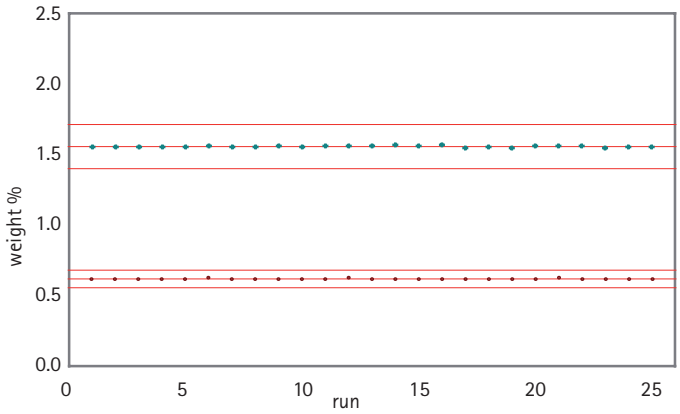

Figure 3. Repeatability of aromatic content (benzene below, toluene above) of naphtha (3). Boundary lines indicate 10% variation limits.

A light naphtha (1) was also analyzed. This naphtha was somewhat lighter than naphtha (3). The chromatogram is shown in Figure 4.

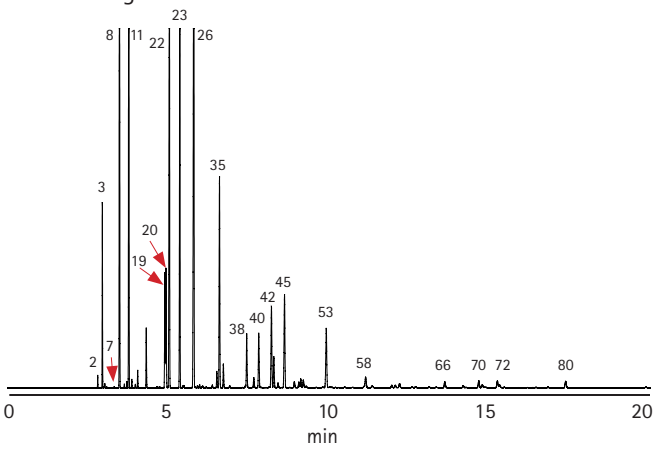

Figure 4. Light naphtha (1).

Light naphtha (1) was also analyzed many times in a repeatability trial. A summary of the results is shown in Figure 5 and Table 6.

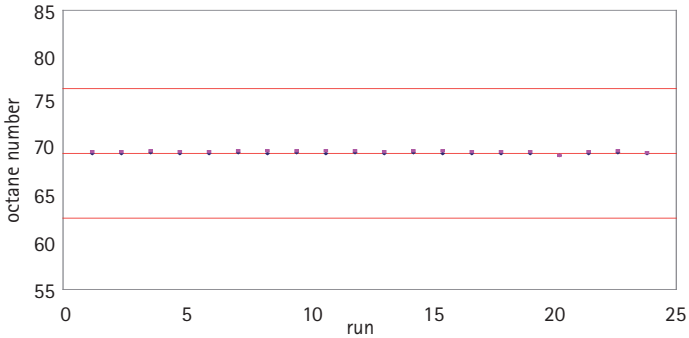

Figure 5. Repeatability data of MON (blue) and RON (red) values of light

naphtha (1). Boundary lines indicate 10% variation limits.

Table 6. Summary results of analysis of light naphtha (1)

Naphtha(1) Run	MON	RON	Density (gr/mL)	Hexane Wt%	Heptane Wt%	Benzene Wt%	Toluene Wt%
1	69.6	69.8	0.6619	12.73	1.70	0.97	0.20
2	69.6	69.8	0.6619	12.75	1.70	0.96	0.20
3	69.7	69.9	0.6619	12.70	1.69	0.96	0.19
4	69.6	69.8	0.6621	12.74	1.70	0.97	0.20
5	69.6	69.8	0.6620	12.74	1.70	0.97	0.20
6	69.7	69.9	0.6620	12.73	1.70	0.95	0.20
7	69.6	69.9	0.6619	12.74	1.70	0.96	0.20
8	69.7	69.9	0.6620	12.75	1.71	0.97	0.20
9	69.6	69.9	0.6620	12.74	1.71	0.96	0.20
10	69.7	69.9	0.6620	12.75	1.70	1.03	0.20
11	69.6	69.8	0.6624	12.82	1.73	1.04	0.20
12	69.7	69.9	0.6618	12.72	1.70	0.95	0.20
13	69.6	69.9	0.6619	12.75	1.71	0.96	0.20
14	69.6	69.8	0.6620	12.74	1.71	0.95	0.20
15	69.6	69.8	0.6621	12.78	1.72	0.96	0.20
16	69.6	69.8	0.6620	12.75	1.70	0.96	0.20
17	69.4	69.4	0.6601	12.85	1.72	0.96	0.20
18	69.6	69.8	0.6619	12.72	1.70	0.95	0.20
19	69.7	69.9	0.6622	12.70	1.69	1.05	0.19
20	69.6	69.7	0.6622	12.81	1.72	0.97	0.20
Average	69.62	69.82	0.6619	12.751	1.706	0.973	0.199
St.dev.	0.070	0.12	0.0004	0.038	0.011	0.030	0.0031
RSD%	0.10	0.16	0.07	0.30	0.62	3.09	1.55

It can be seen from Figure 5 that excellent repeatability was again achieved. The individual analysis results are virtually on the average line.

The results of the analysis of another light naphtha sample (2) are shown in Figure 6.

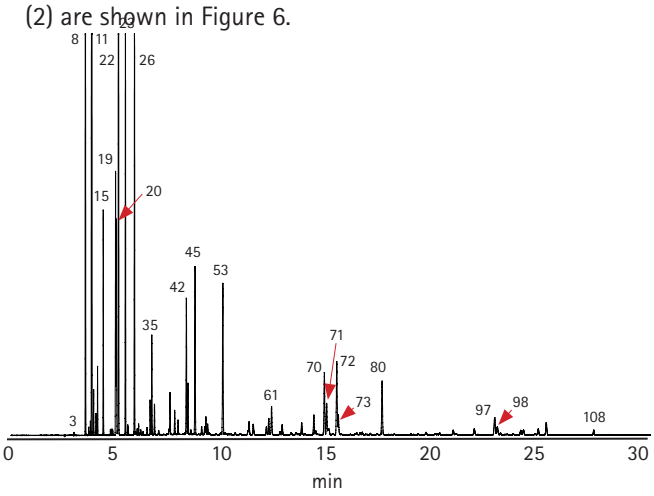

Figure 6. Light naphtha (2).

The repeatability data for naphtha (2) are presented in Table 7 and Figure 7.

Table 7. Summary results of analysis of light naphtha (2)

Naphtha(2) Run	MON	RON	Density (gr/mL)	Pentane Wt%	Hexane Wt%	Heptane Wt%	Benzene Wt%
1	70.0	68.2	0.6507	49.55	3.58	1.90	0.37
2	69.9	68.1	0.6504	49.52	3.59	1.91	0.37
3	69.9	68.1	0.6505	49.42	3.60	1.92	0.37
4	69.9	68.1	0.6505	49.37	3.60	1.92	0.37
5	69.8	68.1	0.6507	49.24	3.59	1.92	0.37
6	69.9	68.1	0.6507	49.37	3.58	1.91	0.36
7	69.9	68.1	0.6506	49.46	3.59	1.92	0.37
8	69.9	68.1	0.6510	49.21	3.60	1.93	0.37
9	69.9	68.1	0.6505	49.49	3.56	1.89	0.36
10	69.9	68.1	0.6506	49.41	3.58	1.90	0.36
11	70.3	68.7	0.6524	49.14	3.57	1.90	0.36
12	69.9	68.2	0.6504	49.51	3.59	1.91	0.37
13	70.0	68.2	0.6503	49.68	3.57	1.89	0.36
14	69.2	67.2	0.6515	49.39	3.59	1.91	0.36
15	69.8	68.1	0.6506	49.30	3.59	1.91	0.36
16	69.9	68.1	0.6506	49.40	3.58	1.91	0.37
17	69.0	67.0	0.6513	49.27	3.57	1.90	0.36
18	70.0	68.2	0.6508	49.44	3.57	1.90	0.36
19	70.1	68.4	0.6509	49.48	3.59	1.91	0.36
20	69.0	67.0	0.6514	49.26	3.59	1.92	0.36
21	69.9	68.1	0.6505	49.40	3.58	1.90	0.37
22	70.0	68.3	0.6505	49.59	3.58	1.90	0.36
23	69.9	68.1	0.6505	49.48	3.57	1.90	0.36
24	69.8	68.1	0.6507	49.30	3.59	1.91	0.37
25	69.8	68.1	0.6507	49.24	3.59	1.92	0.37
Average	69.824	68.036	0.651	49.397	3.584	1.908	0.364
St.dev.	0.31	0.39	0.0005	0.13	0.011	0.010	0.0050
RSD%	0.44	0.57	0.070	0.26	0.30	0.54	1.38

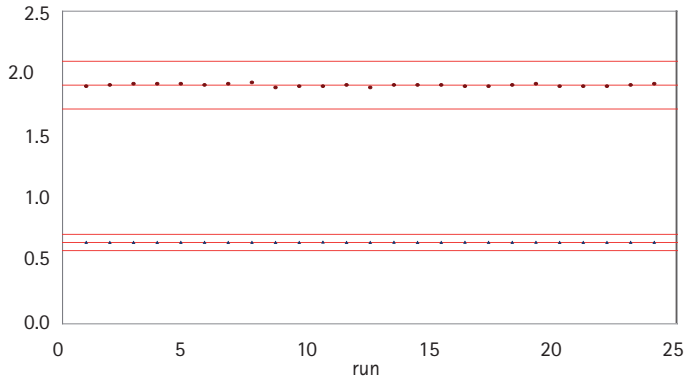

Figure 7. Repeatability data on density (g/mL, below) and heptane content (wt%, above) of light naphtha (2). Boundary lines indicate 10% variation limits.

The repeatability data in Table 7 and Figure 7 are impressive. The individual results adhere very closely to the mean. A proven feature of the DHA software is peak assignment based corrected retention times. This is important, especially when overloaded peaks are present (Figure 8).

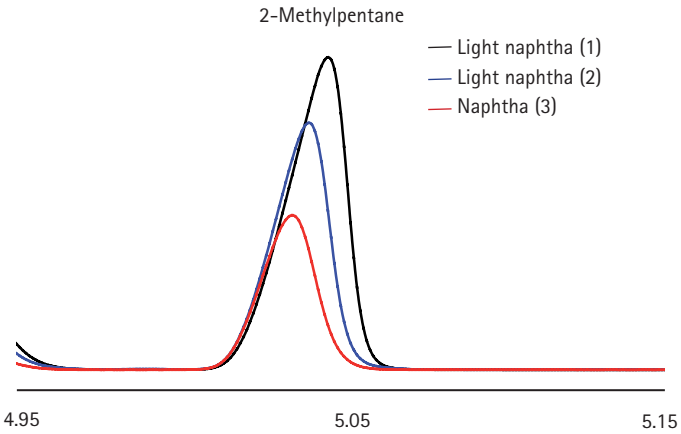

Figure 8. Overlay of chromatograms from three naphtha samples (magnified portion).

Table 8. Corrected retention times and asymmetry factors

	Tr (min)	Corr. Tr (min)	As. factor
Light naphtha (1)	5.046	5.02	0.44
Light naphtha (2)	5.040	5.02	0.62
Naphtha (3)	5.035	5.02	0.80

From Figure 8 and Table 8 it is clear that overloaded peaks show shifted retention times. The risk of mis-identification is high. Galaxie and DHA software overcome this problem by calculating the corrected retention times based on the peak asymmetry and the derived retention indices.

Conclusion

The Varian 450-GC based Detailed Hydrocarbon Analyzer is specially designed for analyzing individual hydrocarbon components, as well as oxygenates present in spark ignition fuels and light hydrocarbon streams such as naphtha. If the system is equipped with a 40 m x 0.1 mm CP-Sil PONA CB column from Varian, Inc., analysis times are significantly reduced while maintaining separation power and ensuring analytical results of high quality.

Being able to calculate corrected retention times is a real benefit when using narrow bore columns. Peaks from sample components present in large amounts tend to show overloading and thus retention time shifting. The DHA software calculates the corrected retention time based on peak skewing, ensuring correct peak assignment.

The DHA analyzer yields all required reports. A detailed hydrocarbon analysis report gives, per component, the content in weight% and volume% as well as (corrected) retention times and retention index. PIONA reports can be generated, again in weight% and or volume%, where sample components are grouped in chemical classes e.g. iso-, cyclic- and normal paraffins and olefins, aromatics and oxygenates.

In conclusion, a sample properties report can be generated which gives the MON and RON values, as well as read vapor pressure, density, net heat and gross heat, and a boiling point distribution. This fast DHA system is perfectly capable of analyzing relative light hydrocarbon streams such as naphtha. Peak identification via retention index and comparison with a database proved to be a very powerful methodology.

References

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These data represent typical results.
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Varian, Inc.
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